CO 2 Solubility in Hybrid Solvents Containing 1-Butyl-3-methylimidazolium tetrafluoroborate and Mixtures of Alkanolamines

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Supporting Information

CO_2 Solubility in Hybrid Solvents Containing 1-Butyl-3-methylimidazolium tetrafluoroborate and Mixtures of Alkanolamines

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BUOYANCY CORRECTION AND CALCULATION OF SOLUBILITY

Solubility measurements were corrected by taking into buoyancy effects for liquid samples under different gas pressure, as is typically required for gravimetric measurements with liquid samples due to the significant change in their sample density with pressure. A buoyancy force is caused by the change in sample density upon absorption of a gas, and the surrounding gas being displaced by the presence of the sample, the sample container and balance components in the reactor. These components include the dry sample m_s [g], the mass of gas absorbed m_a [g], the sample container and its associated attachments (hook and chains) represented by m_I [g], the mass of the counterweight m_c [g], the mass of its associated attachments represented by m_{II} [g]. Table S1 contains measured masses and calculated volumes of each of the components explained above.

Table S1: Measured Mass and Calculated Volume of Balance Components used in Gravimetric Analysis

Balance Component	Mass/g	Density/g·cm^{-3}	Volume/cm^3
Sample Container (m_{sc})	0.6194	7.9	0.078
Wire ($m_{I,1}$)	0.063	21	0.003
Chain ($m_{I,2}$)	0.1776	19.3	0.009
Counterweight (m_C)	0.8008	7.9	0.101
Hook ($m_{II,1}$)	0	0	0.000
Chain ($m_{II,2}$)	0.143	19.3	0.007

Uncertainty: u(m) = 0.1 mg

Density of balance components provided by Roper[23] and Roper[24]

The volume of gas displaced is represented by V_I, V_C, and V_{II} accounting for the volume of the sample container and chain, the counterweight, and counterweight chain respectively. The buoyancy force is dependent on the density of the gas at each equilibrium temperature and pressure condition. This force provided a significant source of error in weight reading, since the density of the sample decreased significantly upon uptake of the absorbing gas. This term is represented by V_{as}, the volume of the sample and the absorbed gas.

The weight reading produced by the gravimetric analyser is given by the following equation:

$$W = g[m_s + m_a - m_c + m_I - m_{II} - \rho_f(V_{as} + V_I - V_{II} - V_c)] \qquad \text{(eq S1)}$$

where W is the weight reading in [N], g is acceleration due to gravity in [$m \cdot s^{-2}$], and ρ_f is the density of the absorbing gas [$g \cdot cm^{-3}$].

The density of the samples decreases upon absorption of a gas, making the sample more buoyant and lowering the weight of the sample. Samples thus appear to have a lower mass than they actually have.

The effect of buoyancy was noted, for example, in the data for N_2 gas with Sample 3 MEA:DEA:[Bmim][BF_4] at 33:16.2:50.8 wt% at 303.15 K has been plotted in Figure S1.

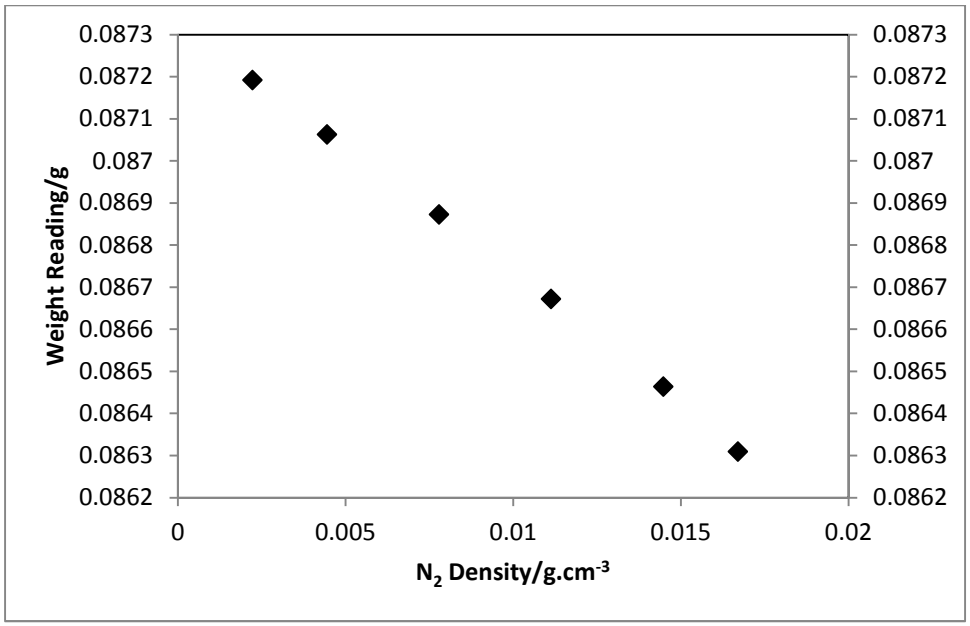

Figure S1: Bouyancy Measurements using N_2 gas for MEA:DEA:[Bmim][BF_4] at 33:16.2:50.8 wt% at 303.15 K

Buoyancy measurements were done using nitrogen gas for all samples, before measuring absorption of CO_2. Nitrogen is a non absorbing gas, which meant that for systems with nitrogen gas, the weight of the sample would not change. Yet as shown Figure S1, higher pressures resulted in lower sample weight readings. This data had to be incorporated into the calculation of the actual CO_2 equilibrium solubility for each sample. Nitrogen was used in this research as it molecular weight is comparable to O_2 and CO_2. Other research in the literature also used helium[20].

Using nitrogen gas, the weight reading of the sample was given by:

$$W = g[m_s + m_{a,N2} - m_c + m_I - m_{II} - \rho_{N2}(V_{N2} + V_I - V_{II} - V_c)] \qquad \text{(eq S2)}$$

where $m_{a,N2}$ is the mass of absorbed nitrogen. $m_{a,N2} = 0$ g.

V_{N2} is the volume of sample and absorbed nitrogen.

Equation above can be rearranged to form a linear equation:

$$\frac{W}{g} = -\rho_{N_2}(V_{N_2} + A) + C \qquad \text{(eq S3)}$$

Where constants $A = V_I - V_{II} - V_C$ and $C = m_S + m_{a,N_2} - m_C + m_I + m_{II}$

$m_{a,N2} = 0$ since absorption of N_2 in the solvents studied in this work is negligible.

By plotting weight reading against N_2 density as shown in Figure 2 and noting the gradient, V_{N2} was found.

It was assumed that V_{as} from (eq S1) is equal to V_{N2} in (eq S2)[25]. This assumption incurs negligible error since N_2 possesses a molecular mass comparable to CO_2, thereby simulating the buoyancy effect of CO_2.

Thus, V_{as} was substituted for V_{N2} in Equation (eq S1) to calculate the mass of gas absorbed (m_a) in systems containing CO_2.

$$m_a = \frac{W}{g} - m_s + \rho_{CO_2}(C + V_{as}) \qquad \text{(eq S4)}$$

Where $V_{as} = V_{N2}$

Equilibrium mole fraction x_{CO2} was found by the following:

$$x_{CO_2} = \frac{\frac{m_a}{MM_{CO_2}}}{\frac{m_a}{MM_{CO_2}} + n_s} \qquad \text{(eq S5)}$$

Where MM_{CO2} is the molar mass of CO_2 and n_s is the moles of the solvent. For hybrid solvents, the moles of each component in the hybrid solvent were calculated and combined since the composition and mass quantity of each component was predetermined during sample preparation. Further details concerning the calculation procedure for buoyancy correction and the

determination of equilibrium CO_2 liquid mole fraction by gravimetric analysis are provided in the work of Osman (2014)[5] as well as in the work of Macedonia et al.[25] and Shiflett et al.[26].

Table S-2: Measured and Modelled Absorption and Desorption Data of CO_2 in MEA:[Bmim][BF_4] at 29.3:70.7 wt%

P_{meas}/MPa	T/K	x_{CO2}	P_{meas}/MPa	T/K	x_{CO2}	*P_{calc}/MPa
Absorption			Desorption			
0.0498	303.74	0.142	0.0496	303.18	0.140	0.1125
0.1000	303.18	0.159	0.0996	303.20	0.157	0.1685
0.3999	303.17	0.182	0.3993	303.23	0.182	0.4531
0.6997	303.18	0.200	0.6996	303.21	0.199	0.7362
1.0001	303.20	0.217	0.9995	303.21	0.215	1.0641
1.2998	303.11	0.232	1.2977	303.23	0.228	1.2596
1.5001	303.17	0.242	1.4999	303.18	0.241	1.4053
0.0498	313.16	0.122	0.0499	313.22	0.122	0.1176

0.1000	313.15	0.126	0.0999	313.08	0.126	0.1816
0.3999	313.12	0.142	0.4048	313.25	0.142	0.3894
0.6998	313.11	0.156	0.7144	313.24	0.156	0.6965
1.0001	313.17	0.170	0.9999	313.22	0.170	0.9361
1.3000	313.15	0.184	1.3127	313.25	0.184	1.1369
1.5000	313.12	0.192	1.5003	313.25	0.192	1.3069
0.0498	323.18	0.079	0.0545	323.27	0.079	0.0197
0.0998	323.15	0.087	0.1351	323.22	0.087	0.0463
0.3999	323.11	0.124	0.4489	323.20	0.124	0.4290
0.7000	323.13	0.138	0.6675	323.14	0.138	0.6661
1.0000	323.21	0.151	1.0188	323.24	0.151	1.1265
1.3000	323.23	0.160	1.3150	323.09	0.160	1.2381
1.5001	323.13	0.171	1.4925	323.17	0.171	1.5705

*P_{Calc} obtained using RK-EOS and Posey-Tapperson-Rochelle model with regressed parameters

Standard Uncertainty: $u(T) = 0.01$ K; $u(P) = 1.25 \times 10^{-4}$ MPa; $u(x) = 0.001$

Table S-3: Measured and Modelled Absorption and Desorption Data of CO_2 in MEA:DEA:[Bmim][BF_4] at 33:16.2:50.8 wt%

P_{meas}/MPa	T/K	x_{CO2}	P_{meas}/MPa	T/K	x_{CO2}	*P_{calc}/MPa
Absorption			Desorption			
0.0498	303.16	0.100	0.0498	303.17	0.100	0.0833
0.1000	303.17	0.104	0.0995	303.18	0.102	0.1472
0.3999	303.20	0.121	0.3991	303.20	0.120	0.3973
0.6999	303.18	0.137	0.6983	303.17	0.133	0.7008
0.9999	303.19	0.153	0.9988	303.16	0.151	1.0652
1.3000	303.17	0.166	1.2999	303.17	0.166	1.3398
1.5001	303.21	0.170	1.4985	303.20	0.170	1.3653

0.0497	313.20	0.100	0.0498	313.15	0.101	0.1107
0.0999	313.10	0.103	0.0999	313.09	0.103	0.1632
0.3999	313.14	0.115	0.3999	313.16	0.114	0.3344
0.6999	313.20	0.131	0.7000	313.14	0.129	0.6877
0.9999	313.11	0.144	0.9999	313.15	0.143	1.0127
1.2999	313.15	0.158	1.3000	313.10	0.158	1.4052
1.4999	313.10	0.162	1.5000	313.13	0.161	1.4535
0.0498	323.14	0.096	0.0498	323.13	0.098	0.0850
0.0999	323.16	0.098	0.0998	323.16	0.101	0.1193
0.3999	323.13	0.112	0.3993	323.12	0.109	0.3439
0.7000	323.16	0.125	0.7000	323.13	0.127	0.6012
0.9999	323.20	0.139	0.9999	323.17	0.141	1.0734
1.2998	323.21	0.149	1.2999	323.12	0.152	1.2938
1.5000	323.15	0.155	1.4999	323.16	0.154	1.4657

*P_{Calc} obtained using RK-EOS and Posey-Tapperson-Rochelle model with regressed parameters

Standard Uncertainty: $u(T) = 0.01$ K; $u(P) = 1.25 \times 10^{-4}$ MPa; $u(x) = 0.001$

Table S-4: Measured and Modelled Absorption and Desorption Data of CO_2 in MEA:DEA:[Bmim][BF_4] at 31.8:12.1:56.1 wt%

P_{meas}/MPa	T/K	x_{CO2}	P_{meas}/MPa	T/K	x_{CO2}	*P_{calc}/MPa
Absorption			Desorption			
0.0499	303.16	0.210	0.0498	303.21	0.208	0.1157
0.0999	303.19	0.214	0.1000	303.12	0.210	0.1853
0.3999	303.17	0.229	0.3999	303.14	0.225	0.4003
0.6999	303.18	0.245	0.6999	303.17	0.240	0.7090
1.0000	303.14	0.257	0.9999	303.25	0.254	1.0251
1.3000	303.17	0.270	1.2999	303.21	0.267	1.3782
1.5000	303.23	0.273	1.4999	303.20	0.273	1.3842

0.0498	313.07	0.196	0.0497	313.28	0.192	0.1072
0.0999	313.13	0.200	0.1000	313.05	0.203	0.1639
0.3999	313.17	0.219	0.3999	313.23	0.215	0.4194
0.6999	313.15	0.229	0.6999	313.25	0.224	0.7122
1.0000	313.23	0.238	1.0000	313.08	0.234	0.8860
1.3000	313.15	0.248	1.3001	313.11	0.245	1.1213
1.5000	313.21	0.252	1.5000	313.15	0.253	1.2930
0.0498	323.14	0.172	0.0497	323.27	0.168	0.0745
0.0999	323.11	0.174	0.0999	323.22	0.169	0.0975
0.3998	323.13	0.194	0.3999	323.20	0.190	0.3916
0.6999	323.12	0.212	0.6999	323.14	0.208	0.6549
1.0001	323.14	0.226	1.0001	323.24	0.222	0.9096
1.2999	323.18	0.240	1.3000	323.09	0.245	1.3182
1.4999	323.10	0.249	1.5000	323.17	0.250	1.7179

*P_{Calc} obtained using RK-EOS and Posey-Tapperson-Rochelle model with regressed parameters

Standard Uncertainty: $u(T) = 0.01$ K; $u(P) = 1.25 \times 10^{-4}$ MPa; $u(x) = 0.001$

Table S-5: Measured and Modelled Absorption and Desorption Data of CO_2 in MEA:MDEA:[Bmim][BF_4] at 31.6:10.4:58 wt%

P_{meas}/MPa	T/K	x_{CO2}	P_{meas}/MPa	T/K	x_{CO2}	*P_{calc}/MPa
Absorption			Desorption			
0.0498	303.15	0.187	0.0498	303.18	0.189	0.1902
0.0999	303.15	0.195	0.0998	303.20	0.197	0.2571
0.4000	303.19	0.213	0.3993	303.23	0.216	0.4288
0.6997	303.17	0.233	0.7000	303.21	0.235	0.6489
0.9998	303.25	0.247	0.9999	303.21	0.249	0.9309
1.3000	303.18	0.261	1.2999	303.23	0.261	1.2431
1.5001	303.14	0.272	1.4999	303.18	0.272	1.4478

0.0499	313.16	0.177	0.0499	313.15	0.179	0.2892
0.0999	313.18	0.180	0.0999	313.09	0.183	0.3309
0.3997	313.14	0.199	0.4048	313.16	0.202	0.4535
0.6999	313.15	0.218	0.7144	313.14	0.221	0.7421
1.0001	313.13	0.232	0.9999	313.15	0.231	1.0920
1.2998	313.17	0.249	1.3127	313.10	0.249	1.3510
1.5001	313.15	0.257	1.5003	313.13	0.257	1.5597
0.0498	323.13	0.143	0.0499	313.27	0.145	0.1978
0.0999	323.16	0.146	0.1000	323.14	0.148	0.2328
0.4000	323.12	0.164	0.4000	323.16	0.166	0.4211
0.6999	323.13	0.181	0.7000	323.25	0.183	0.6226
1.0000	323.17	0.195	1.0000	323.22	0.197	0.9594
1.2999	323.12	0.206	1.3000	323.23	0.206	1.1188
1.5001	323.16	0.216	1.4999	323.10	0.216	1.3285

*P_{Calc} obtained using RK-EOS and Posey-Tapperson-Rochelle model with regressed parameters

Standard Uncertainty: $u(T) = 0.01$ K; $u(P) = 1.25 \times 10^{-4}$ MPa; $u(x) = 0.001$

Table S-6: Measured and Modelled Absorption and Desorption Data of CO_2 in MEA:MDEA:[Bmim][BF_4] at 30.3:21.8:48 wt%

P_{meas}/MPa	T/K	x_{CO2}	P_{meas}/MPa	T/K	x_{CO2}	*P_{calc}/MPa
Absorption			Desorption			
0.0498	303.25	0.184	0.0499	303.74	0.186	0.2204
0.0999	303.19	0.192	0.1000	303.18	0.194	0.2773
0.3998	303.17	0.213	0.4000	303.17	0.216	0.4580
0.6999	303.19	0.235	0.7000	303.18	0.238	0.7069
0.9999	303.21	0.253	1.0000	303.20	0.256	0.9809
1.2999	303.24	0.260	1.3000	303.11	0.264	1.0830
1.5001	303.19	0.274	1.4999	303.17	0.277	1.3943

0.0498	313.16	0.141	0.0499	313.07	0.143	0.2024
0.0999	313.17	0.144	0.1000	313.13	0.146	0.2274
0.3999	313.12	0.171	0.4000	313.17	0.173	0.4202
0.6999	313.17	0.194	0.7000	313.15	0.196	0.6578
0.9999	313.15	0.215	0.9998	313.23	0.213	0.9566
1.2999	313.14	0.234	1.3001	313.15	0.237	1.3392
1.5002	313.05	0.249	1.4999	313.21	0.246	1.7603
0.0498	323.13	0.080	0.0498	323.13	0.080	0.1272
0.0999	323.15	0.086	0.0999	323.16	0.087	0.1558
0.3999	323.14	0.124	0.3999	323.12	0.125	0.3631
0.6999	326.53	0.151	0.7000	323.13	0.154	0.7171
0.9992	325.56	0.167	0.9999	323.17	0.170	0.9110
1.3000	320.47	0.195	1.3000	323.12	0.193	1.0656
1.4999	323.07	0.206	1.5000	323.16	0.204	1.4933

*P_{Calc} obtained using RK-EOS and Posey-Tapperson-Rochelle model with regressed parameters

Standard Uncertainty: $u(T) = 0.01$ K; $u(P) = 1.25 \times 10^{-4}$ MPa; $u(x) = 0.001$

Table S-7: Measured and Modelled Absorption and Desorption Data of CO_2 in MEA:DEA:MDEA:[Bmim][BF_4] at 29.8:11.7:12.8:45.7 wt%

P_{meas}/MPa	T/K	x_{CO2}	P_{meas}/MPa	T/K	x_{CO2}	*P_{calc}/MPa
Absorption			Desorption			
0.0498	303.19	0.143	0.0498	303.21	0.142	0.1410
0.1000	303.18	0.148	0.1000	303.12	0.147	0.1757
0.3999	303.16	0.172	0.3999	303.14	0.171	0.4329
0.6999	303.18	0.191	0.6997	303.17	0.190	0.7120
0.9999	303.17	0.208	1.0001	303.25	0.205	1.0146
1.2999	303.24	0.219	1.2998	303.21	0.216	1.2066
1.4999	303.20	0.228	1.5001	303.20	0.231	1.3930

0.0498	313.15	0.132	0.0498	313.15	0.132	0.1122
0.0999	313.14	0.140	0.0999	313.09	0.141	0.1626
0.3999	313.16	0.169	0.3999	313.16	0.169	0.5062
0.6998	313.14	0.183	0.6999	313.14	0.182	0.7397
0.9999	313.16	0.197	0.9999	313.15	0.199	1.0174
1.3000	313.18	0.211	1.2999	313.10	0.213	1.3487
1.4995	313.14	0.221	1.5002	313.13	0.221	1.6216
0.0498	323.13	0.115	0.0499	323.23	0.113	0.0640
0.0999	323.13	0.118	0.0999	323.12	0.117	0.0726
0.3999	323.15	0.144	0.3999	323.12	0.145	0.3555
0.6999	323.15	0.166	0.6999	323.11	0.167	0.5417
1.0001	323.15	0.186	1.0000	323.11	0.184	0.9613
1.3000	323.21	0.199	1.3000	323.10	0.202	1.2671
1.5000	323.18	0.207	1.5000	323.10	0.205	1.4935

*P_{Calc} obtained using RK-EOS and Posey-Tapperson-Rochelle model with regressed parameters

Standard Uncertainty: $u(T) = 0.01$ K; $u(P) = 1.25 \times 10^{-4}$ MPa; $u(x) = 0.001$

Table S-8: Binary Interaction and Fitting Parameters for Predicting CO_2 Absorption in Hybrid Solvents using the Posey-Tapperson-Rochelle Model with RK-EOS

System	$ß_0$	$ß_1$	ℓ_{12}	ℓ_{21}	τ_{12}	m_{12}	A	B	C	D	Root* Mean Square Error (%)
CO_2 in [Bmim][BF_4] + MEA at 70.7:29.3 wt%	0.294	-0.056	3.92E+9	0.384	114.203	5.449	14.343	-1.53E03	-4.79E05	9.37E03	6.898
CO_2 in MEA+DEA+[Bmim][BF_4] at 33:16.2:50.8 wt%	0.322	-0.069	1.836	0.641	1.52E03	8.241	-48.458	-939.819	-5.05E05	1.11E04	5.878
CO_2 in MEA+DEA+[Bmim][BF_4] at 31.8:12.1:56.1 wt%	0.293	-0.056	1.306	0.621	490.964	8.818	-8.106	-4.59E03	-1.04E05	3.79E03	6.446
CO_2 in MEA+MDEA+[Bmim][BF_4] at 31.6:10.4:58 wt%	0.257	-0.042	1.001	0.996	8.339	874.592	22.422	-6.60E03	-1.18E03	689.279	7.437
CO_2 in MEA+MDEA+[Bmim][BF_4] at 30.3:21.8:48 wt%	1.275	-0.384	0.299	9.11E12	-45.282	7.078	33.478	-8.11E03	3.05E04	-264.42	7.729
CO_2 in MEA+DEA+MDEA+[Bmim][BF_4] at 29.8:11.7:12.8:45.7 wt%	-5.04E-6	1.23E-6	1.13E13	21.322	-184.519	1.069	-6.894	-2.03E03	-9.96E04	3.04E03	7.482

*Root Mean Square Error for each system was calculated neglecting data measured at 0.05 and 0.1 MPa.